CHAPTER 2
PRINCIPLES OF OPERATION AND THEORY

2-1. Types of Adsorption Media.

 a. *Activated Carbon*. Activated carbon can be manufactured from carbonaceous material, in-cluding coal (bituminous, subbituminous, and lignite), peat, wood, or nutshells (i.e., coconut). The manufacturing process consists of two phases, carbonization and activation. The carboniza-tion process includes drying and then heating to separate by-products, including tars and other hydrocarbons, from the raw material, as well as to drive off any gases generated. The carboni-zation process is completed by heating the material at 400–600°C in an oxygen-deficient atmos-phere that cannot support combustion.

 (1) *General*. The carbonized particles are "activated" by exposing them to an activating agent, such as steam at high temperature. The steam burns off the decomposition products from the carbonization phase to develop a porous, three-dimensional graphite lattice structure. The size of the pores developed during activation is a function of the time that they are exposed to the steam. Longer exposure times result in larger pore sizes. The most popular aqueous phase car-bons are bituminous based because of their hardness, abrasion resistance, pore size distribution, and low cost, but their effectiveness needs to be tested in each application to determine the opti-mal product. The three-dimensional graphite lattice pore structure of a typical activated carbon particle is shown in Figure 2-1.

 (2) *Powdered Activated Carbon (PAC).* PAC is made up of crushed or ground carbon particles, 95–100% of which will pass through a designated mesh sieve or sieves. The American Water Works Association Standard (AWWA, 1997) defines GAC as being retained on a 50-mesh sieve (0.297 mm) and PAC material as finer material, while American Society for Testing and Materials (ASTM D5158) classifies particle sizes corresponding to an 80-mesh sieve (0.177 mm) and smaller as PAC. PAC is not commonly used in a dedicated vessel, owing to the high headloss that would occur. PAC is generally added directly to other process units, such as raw water intakes, rapid mix basins, clarifiers, and gravity filters.

 (3) *Granular Activated Carbon (GAC).* GAC can be either in the granular form or ex-truded. GAC is designated by sizes such as 8×20, 20×40, or 8×30 for liquid phase applica-tions and 4×6, 4×8 or 4×10 for vapor phase applications. A 20×40 carbon is made of parti-cles that will pass through a U.S. Standard Mesh Size No. 20 sieve (0.84 mm) (generally speci-fied as >85% passing) but be retained on a U.S. Standard Mesh Size No. 40 sieve (0.42 mm) (generally specified as >95% retained). AWWA (1992) B604 uses the 50-mesh sieve (0.297 mm) as the minimum GAC size. The most popular aqueous phase carbons are the 12×40 and 8×30 sizes because they have a good balance of size, surface area, and headloss characteristics.

100 Angstrom

Graphite Platelet

Aliphatic Dislocation of Platelet

Interbonding of Platelets

(Atom) Part of a molecule

London Disperson Force
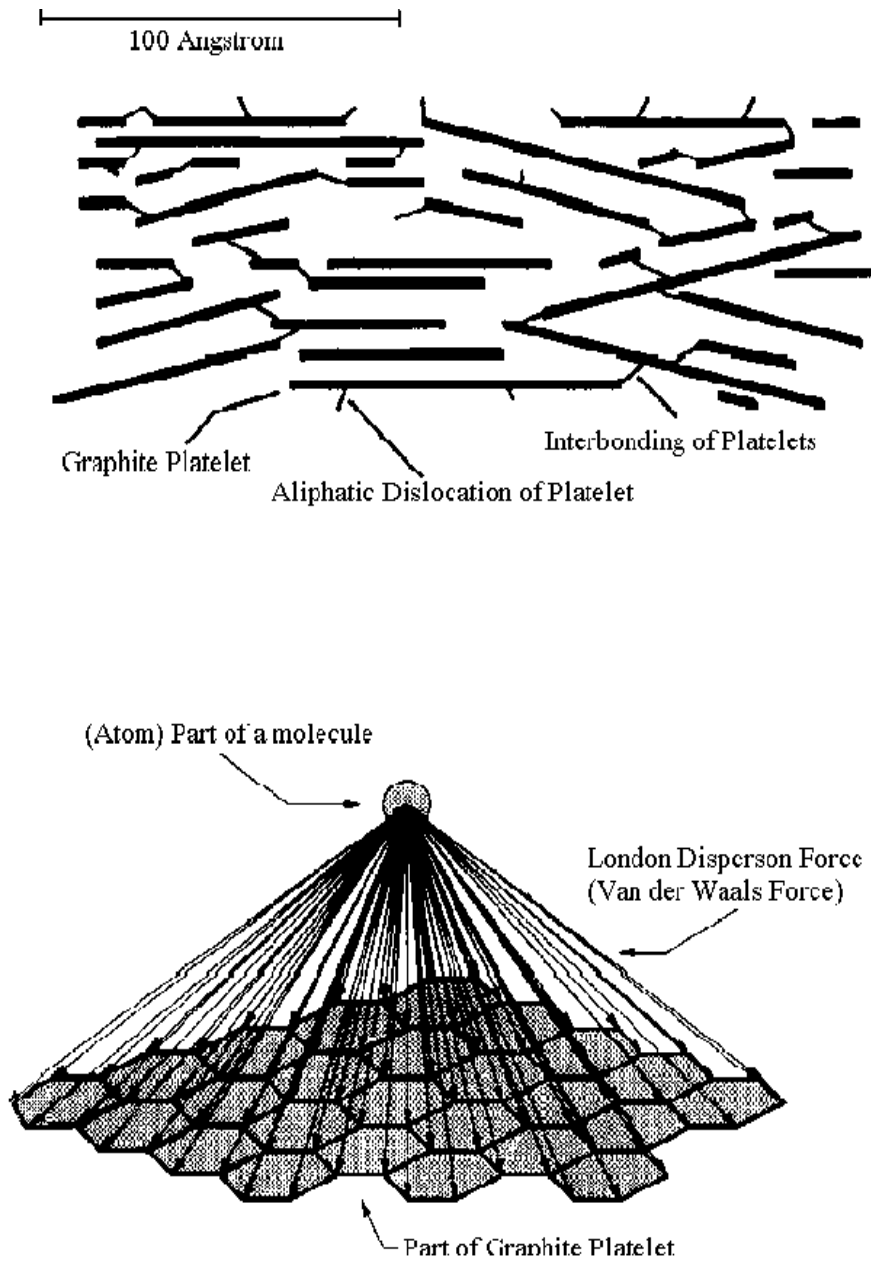(Van der Waals Force)

Part of Graphite Platelet

Figure 2-1. Activated carbon structure.

The 12×40 carbon is normally recommended for drinking water applications where the water contains a low suspended solid content. The 8×30 size is the most commonly used for most applications (Appendix D, Carbonair).

   b. Non-carbon. Many alternative adsorption media are in general service today for removing organic constituents from vapor and liquid streams. Organically modified clays, polymeric adsorbents, and zeolite molecular sieves are the primary non-activated-carbon adsorbents currently used in hazardous waste treatment (Black & Veatch, 1998). See paragraph 3-3 for additional information.

2-2. Properties of Granular Activated Carbon. Granular activated carbon properties are defined in ASTM D2652. In addition to these properties, the following paragraphs provide additional information.

   a. Particle Size Distribution. A standard test procedure for particle size distribution (PSD) is defined in ASTM D2862. Information derived from this test is used to specify the carbon particle size uniformity. Two particle size criteria are the effective size, which corresponds to the sieve size through which 10% of the material will pass, and the uniformity coefficient, which is the ratio of the sieve size that will just pass 60% of the material to the effective size. Generally, the rate of adsorption will increase as the particle size decreases, as the process step of diffusion to the carbon surface should be enhanced by the smaller particles. Note that another critical aspect of rate of adsorption is the pore size distribution, and development of "transport pores" within the particle that allow effective migration of contaminants to the point of adsorption. However, particle size may not be that important in all cases, as the porous nature of the carbon particles results in large surface areas in all sizes of carbon particles. Headloss through a carbon bed increases as the carbon particle size decreases and as the uniformity coefficient increases.

   b. Surface Area. Surface area is the carbon particle area available for adsorption. In general, the larger the surface area is, the greater is the adsorption capacity; however, this surface area needs to be effective. And a high degree of the area needs to be in the "adsorption pore" region, as well as being accessible to the contaminant with an effective "transport pore" structure, for the capacity to be useful. This is measured by determining the amount of nitrogen adsorbed by the carbon and reported as square meters per gram (commonly between 500 and 2000 m^2/g). ASTM D 3037 identifies the procedure for determining the surface area using the nitrogen BET (Brunauer, Emmett, and Teller) method. Nitrogen is used because of its small size, which allows it to access the micropores within the carbon particle.

   c. Pore Volume. The pore volume is a measure of the total pore volume within the carbon particles in cubic centimeters per gram (cm^3/g).

   d. Iodine Number. The iodine number refers to the milligrams of a 0.02 normal iodine solution adsorbed during a standard test (ASTM D4607). The iodine number is a measure of the

volume present in pores from 10 to 28 Å (10^{-10} m) in diameter. Carbons with a high percentage of pore sizes in this range would be suitable for adsorbing lower molecular weight substances from water. Carbons with a high iodine number are the most suitable for use as vapor phase carbons, as water molecules tend to effectively block off and isolate pore sizes less than 28 Å. This restricts mass transfer in the micropores, resulting in poor carbon utilization and excessive cost. Virgin liquid phase carbons generally have an iodine number of 1000. Reactivated liquid phase carbon has an iodine number between 800 and 900.

e. Molasses Number. The molasses number refers to the milligrams of molasses adsorbed during the standard test. The molasses number is a measure of the volume in pores greater than 28 Å in diameter. A carbon with a high percentage of this size pore is suitable for adsorbing high molecular weight substances such as color bodies or other colloids. Carbons with a high molasses number are generally used for decolorizing process liquids. As such, the molasses number specification is generally only used in color removal applications, and is not a valid specification requirement for water treatment. This is a proprietary test, and should not be used in specifying GAC.

f. Abrasion Number. The abrasion number measures the ability of carbon to withstand handling and slurry transfer. Two different tests are used, based on the type of carbon material. A Ro Tap abrasion test is used for bituminous-coal-based GAC, and a stirring abrasion test is used for the softer, lignite-coal-based GAC. The abrasion number is the ratio of the final average (mean) particle diameter to the original mean particle diameter (determined by sieve analyses) times 100. The desired average particle size of the GAC retained should be greater than or equal to 70%. This is of limited value because measuring techniques are not reproducible. Procedures are given in AWWA (1997) B604.

g. Apparent Density. The apparent density is equal to the mass (weight) of a quantity of carbon divided by the volume it occupies (including pore volume and interparticle voids, adjusted for the moisture content). Generally, bituminous-based GAC has a density between 28–40 pounds per cubic foot (pcf), lignite-based GAC has a density of approximately 22–26 pcf, and wood-based GAC has a density of 15–19 pcf (AWWA, 1997).

h. Bulk Density. The bulk density is the unit weight of the carbon within the adsorber. Generally, the bulk density of liquid phase applications is 80–95% of the apparent density and, for vapor phase applications, it is 80–100% of the apparent density. Apparent density is used to determine the volumetric carbon usage rate since the carbon usage rate is typically stated in

$$\frac{mg}{g} \left(\frac{mg \ \ contaminant \ \ removed}{gram \ \ of \ \ carbon} \right) \ .$$

2-3. Isotherms. An isotherm is the relationship that shows the distribution of adsorbate (material adsorbed) between the adsorbed phase (that adsorbed on the surface of the adsorbent) and the solution phase at equilibrium. Media manufacturers are a source of adsorption isotherms. Many manufacturers are continuing to conduct research on their products and can often supply chemical-specific adsorption isotherms for their products. However, many of these company isotherms are batch isotherms used as proof of concept data (i.e., to show that a particular product can adsorb a particular chemical). Actual working adsorption capacity may be much less than equilibrium batch capacity because other constituents may be present in water, such as total organic carbon, and because of the non-instantaneous adsorption kinetics. So, you should carefully check manufacturer's data and use them with caution when designing an adsorption system. The designer should also ask the manufacturer for contacts at installations using the media, so that scale-up factors and common operational problems can be investigated.

a. GAC Isotherms. There are three generally recognized mathematical relationships that were developed to describe the equilibrium distribution of a solute between the dissolved (liquid) and adsorbed (solid) phases. These relationships help interpret the adsorption data obtained during constant temperature tests, referred to as adsorption isotherms.

- The Langmuir isotherm equation assumes that fixed individual sites exist on the surface of the adsorbent, each of these sites being capable of adsorbing one molecule, resulting in a layer one molecule thick over the entire carbon surface. The Langmuir model also assumes that all sites adsorb the adsorbate equally.

- The Brunauer, Emmett, and Teller (BET) equation also assumes the adsorbent surface is composed of fixed individual sites. However, the BET equation assumes that molecules can be adsorbed more than one layer thick on the surface of the adsorbent. The BET equation assumes that the energy required to adsorb the first particle layer is adequate to hold the monolayer in place.

- The Fruendlich isotherm equation assumes that the adsorbent has a heterogeneous surface composed of adsorption sites with different adsorption potentials. This equation assumes that each class of adsorption site adsorbs molecules, as in the Langmuir Equation. The Fruendlich Isotherm Equation is the most widely used and will be discussed further.

$$\frac{x}{m} = KC^{\frac{1}{n}}$$

where
       x = amount of solute adsorbed (μg, mg, or g)
       m = mass of adsorbent (mg or g)
       C = concentration of solute remaining in solution after adsorption is complete (at equilibrium) (mg/L)

K, n = constants that must be determined for each solute, carbon type, and temperature.

(1) An example of an isotherm for TCE is presented in Figure 2-2. *K* and 1/*n* or *n* values for multiple contaminant mixtures should be determined by laboratory tests.

(2) Single component isotherms may be used for an order-of-magnitude carbon usage estimate or for determining the feasibility of GAC adsorption using suppliers' literature or previously published literature (Dobbs and Cohen, 1980) for individual compounds. Another source of liquid phase isotherm data constants is the EPA Treatability Database maintained by the National Risk Management Research Laboratory (NRMRL), formerly known as the Risk Reduction Engineering Lab (RREL) (http://www.epa.gov/tdbnrmrl). Vapor phase isotherms are not readily available in the literature.

(3) Some general rules of thumb, uses, and caveats that are helpful in isotherm interpretation are as follows:

- A flat isotherm curve indicates a narrow Mass Transfer Zone (MTZ), meaning that the GAC generally adsorbs contaminants at a constant capacity over a relatively wide range of equilibrium concentrations. Given an adequate capacity, carbons exhibiting this type of isotherm will be very cost effective, and adsorption system design will be simplified owing to a shorter mass transfer zone (see Figure 2-2).

- A steep isotherm curve indicates a wide MTZ, with the adsorption capacity increasing as equilibrium concentration increases. Carbons exhibiting this type of isotherm curve tend to be more cost effective.

- A change in isotherm slope generally occurs for wastes that contain several compounds with variable adsorption capacities. An inflection point occurs when one compound is preferentially adsorbed over another and desorption occurs, so that the preferentially adsorbed compound can utilize sites previously used by less adsorbable compounds (see Figure 2-3).

(4) Isotherms can be developed from data obtained in the laboratory and from existing data sources, such as the National Risk Management Research Laboratory (NRMRL) Treatability Database, texts, and suppliers' literature. A typical example of TCE isotherm data, which was obtained from the NRMRL database, is provided in Figure 2-2. A procedure for calculating an isotherm is included in Appendix C.

b. Polymeric, Clay, Zeolite Molecular Sieve Isotherms. Isotherms for these media are developed in the same way as for carbon media. However, most of the isotherm data for non-carbon adsorption media must be obtained from the manufacturer or from laboratory tests.

2-4. Isotherm Testing. Isotherms are discussed in Paragraph 2-3, and the process for developing an isotherm is addressed in Appendix C. Although the example in Appendix C is specifically developed for a liquid phase application, the vapor phase method is similar. The following paragraphs highlight the types of information that can be obtained from isotherm testing versus column testing. Isotherms are static, equilibrium tests for a given set of conditions. Ideally, isotherms should not be used for the final design of a liquid phase system. Procedures for laboratory development of an isotherm are presented in a variety of texts (Benefield, 1982) or as specified in ASTM D 3860.

   a. Although not advisable for liquid phase applications, published adsorption isotherm data are often used to design vapor phase adsorption systems without bench and pilot testing. For the same contaminant, vapor phase carbon usually has a higher adsorptive capacity than liquid phase carbon, because less adsorptive sites will be taken up by water and humidity. At a 100% relative humidity, the vapor phase carbon's adsorptive capacity will approach the liquid phase carbon adsorptive capacity (Appendix D, Carbonair). However, you should remember that most published isotherm data represent only a single contaminant in a pure medium, and mixed contaminants may behave differently (see Tables 2-1 and 2-2).

   b. One source of published isotherms is the *Adsorption Equilibrium Data Handbook* (Valenzuela and Meyers, 1989). This handbook contains many gas/liquid isotherms. While most of the isotherms are for activated carbon, there are some for carbon molecular sieves, silica gel, and zeolites. A source of information on the Fruendlich isotherm equation is the *Carbon Adsorption Isotherms for Toxic Organics* (Dobbs and Cohen, 1980). This particular source used only a 2-hour test period in lieu of the 24-hour period currently used by industry today. Liquid phase and vapor phase applications are different because the mass transfer characteristics of the two phases are different. The mass transfer kinetics of a contaminant from the vapor phase to the solid phase is nearly instantaneous, while the mass transfer kinetics from the bulk liquid phase to the solid phase is influenced by the presence of the solute, and may be the rate limiting step in some instances. There are four phases to the liquid phase adsorption process. The contaminant must first travel from the bulk liquid phase to the liquid film surrounding the carbon particle. Second, the contaminant must travel through the liquid film surrounding the carbon to the interstitial voids. Third, the contaminant must diffuse through the carbon voids in the carbon solid phase, and fourth, finally adsorb onto the carbon. A more comprehensive discussion of the kinetics of adsorption can be obtained from texts (Faust and Aly, 1987).

RREL Treatability Database   Ver No. 4.0

TRICHLOROETHYLENE
CAS NO: 79-01-6
COMPOUND TYPE: HYDROCARBON, HALOGENATED
FORMULA: C2 H Cl3
CHEMICAL AND PHYSICAL PROPERTIES:
       MOLECULAR WEIGHT: 131.39
       MELTING POINT (C): -84.8
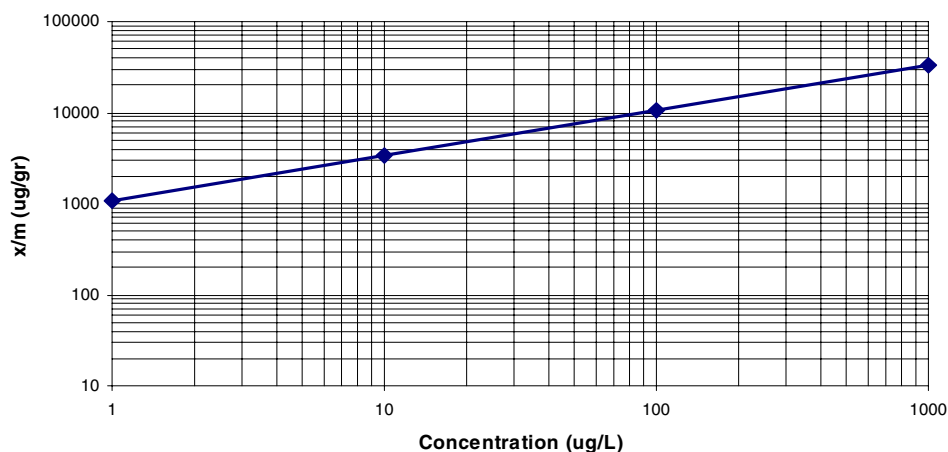   BOILING POINT (C):   86.7
       VAPOR PRESSURE @ T (C), TORR: 77 @ 25
       SOLUBILITY IN WATER @ T (C), MG/L: 1100 @ 25
LOG OCTANOL/WATER PARTITION COEFFICIENT: 2.53
HENRY'S LAW CONSTANT, ATM x M3 MOLE-1: 1.17 E-2 @ 25

ENVIRONMENTAL DATA
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REFERENCE DATABASE
FREUNDLICH ISOTHERM DATA

ADSORBENT	MATRIX	K	1/N	Ce UNITS	X/M UNITS
FILTRASORB 400	C	3390	0.146	µg/L	µg/g
WESTVACO WV-G	C	3260	0.407	µg/L	µg/g
WESTVACO WV-W	C	1060	0.500	µg/L	µg/g
HYDRODARCO 3000	C	713	0.470	µg/L	µg/g
FILTRASORB 300	C	28	0.62	mg/L	mg/g
FILTRASORB 400	C	36.3	0.592	mg/L	mg/g
FILTRASORB 400	C	45	0.625	mg/L	mg/g
FILTRASORB 400	C	2	0.482	µg/L	µg/g

Figure 2-2. Trichloroethylene data.
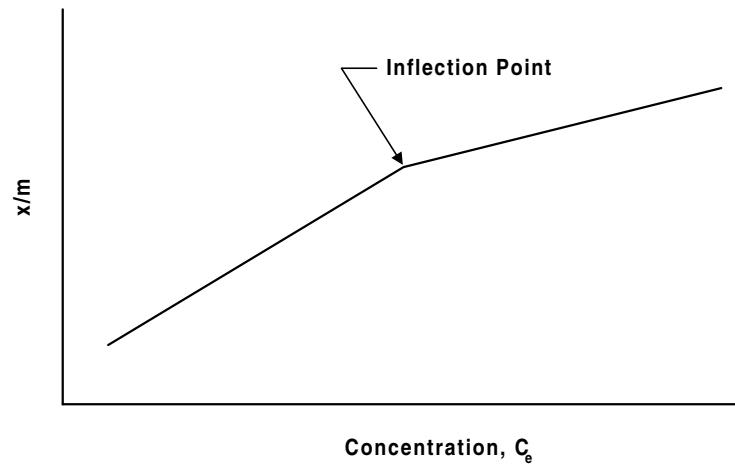
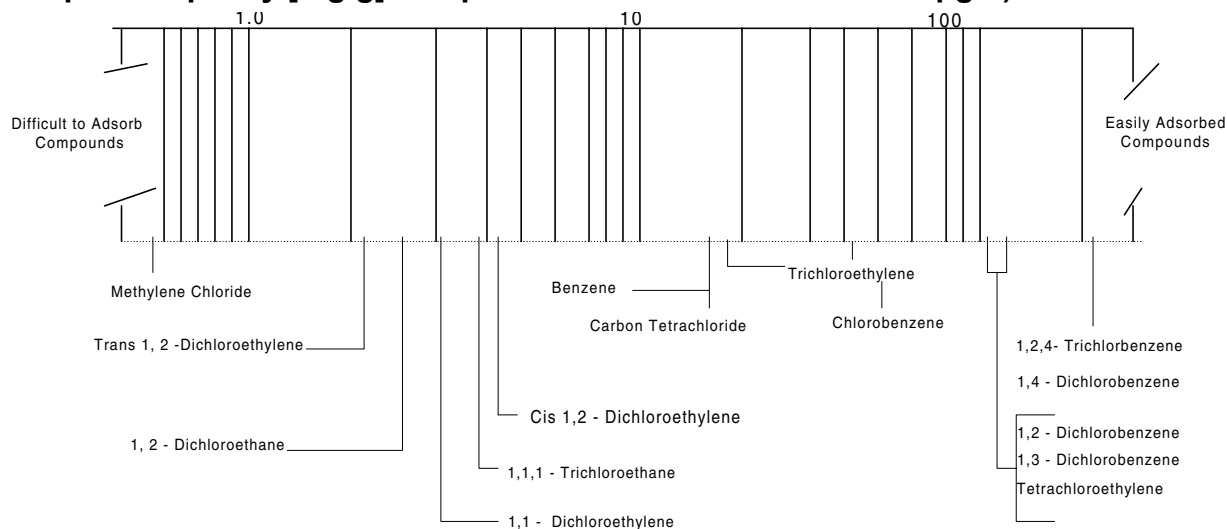**Figure 2-3. Variable capacity adsorption isotherm.**

c. Liquid phase isotherms are useful screening tools for determining the following:

- If adsorption is a viable technology.

- The equilibrium capacity, or approximate capacity at breakthrough, so a preliminary esti-
mate of carbon usage can be made.

- The relative difficulty to remove individual contaminants if single-constituent isotherms
are used, and the identity of the initial breakthrough compound.

- Changes in equilibrium adsorption capacity relative to the concentration of contaminants
in the waste stream, and the effects of changes in waste stream concentration.

- The maximum amount of contaminant that can be adsorbed by GAC at a given
concentration.

- The relative efficiencies of different types of carbons to identify which should be used for
dynamic testing.

d. Liquid phase column testing will provide such data as contact time, bed depth, pre-treat-
ment requirements, carbon dosage, headloss characteristics, and breakthrough curves. Column
testing will also identify how contaminants that are not of regulatory concern, such as iron or
color containing compounds, will affect the efficiency of the treatment process.

Table 2-1
Freundlich adsorption isotherm constants for toxic organic chemicals (mean adsorption capacity [mg/g] at equilibrium concentration of 500 µg/L)

	1.0	10	100

Difficult to Adsorb Compounds

Easily Adsorbed Compounds

Methylene Chloride

Trans 1, 2 -Dichloroethylene

1, 2 - Dichloroethane

Cis 1,2 - Dichloroethylene

1,1,1 - Trichloroethane

1,1 - Dichloroethylene

Benzene

Carbon Tetrachloride

Trichloroethylene

Chlorobenzene

1,2,4- Trichlorbenzene

1,4 - Dichlorobenzene

1,2 - Dichlorobenzene
1,3 - Dichlorobenzene
Tetrachloroethylene

	Freundlich Parameters			Freundlich Parameters		
	K	l/n		K	l/n	
trans-1,2-dichloroethylene				3.1	0.5*	
Benzene	1.0	1.6*				
	16.6	0.4**	1,1-dichloroethylene	4.9	0.5*	
	49.3	0.6†				
	29.5	0.4††	Methylene chloride	1.3	1.2*	
	14.2	0.4§		1.6	0.7***	
Carbon Tetrachloride	11.1	0.8*				
	28.5	0.8†	Tetrachloroethylene	50.8	0.6*	
	38.1	0.7**		84.1	0.4§§	
	25.8	0.7††		273.0	0.6***	
	14.2	0.7§				
	14.8	0.4§§	1,2,4-trichlorobenzene	157.0	0.3*	
Chlorobenzene	91.0	1.0*	1,1,1-trichloroethane	2.5	0.3*	
1,2-dichlorobenzene	129.0	0.4*		9.4	0.5§§	
1,3-dichlorobenzene	118.0	0.4*				
1,4-dichlorobenzene	121.0	0.5*	Trichloroethylene	28.0	0.6*	
	226.0	0.4**		26.2	0.5‡	
1,2-dichloroethene	3.6	0.8*		28.2	0.4§§	
	5.7	0.5§§				
cis-1,2-dichloroethylene	6.5	0.7†	Vinyl chloride	Not Reported		
	8.4	0.5§§				

Freundlich equation:
$$x/m \,(mg/gm) = K \, C \,(mg/1/n)$$

* Filtrasorb ® 300	§ Hydrodarco ® 1030	† Norit
** Filtrasorb ® 400	§§ Witcarb ® 950	†† Nuchar ® WV-G
*** Filtrasorb ® 400		‡ Filtrasorb ® 300

Table 2-2
Freundlich adsorption Isotherm constants for toxic organic compounds† (Dobbs and Cohen 1980)

Compound	K(mg/g)(L/mg)$^{1/n}$	l/n
PCB	14,100	1.03
Bis(2-ethylhexyl phthalate	11,300	1.5
Heptachlor	9,320	0.92
Heptachlor epoxide	2,120	0.75
Butylbenzyl phthalate	1,520	1.26
Toxaphene	950	0.74
Endosulfan sulfate	686	0.81
Endrin	666	0.80
Fluoranthene	664	0.61
Aldrin	651	0.92
PCB-1232	630	0.73
∃ - Endosulfan	615	0.83
Dieldrin	606	0.51
Alachlor	479	0.26
Hexachlorobenzene	450	0.60
Pentachlorophenol	436	0.34
Anthracene	376	0.70
4 – Nitrobiphenyl	370	0.27
Fluorene	330	0.28
Styrene	327	0.48
DDT	322	0.50
2 – Acetylaminofluorene	318	0.12
∀ - BHC	303	0.43
Anethole	300	0.42
3,3 – Dichlorobenzidine	300	0.20
(- BHC (lindane)	285	0.43
2 – Chloronaphthalene	280	0.46
Phenylmercuric acetate	270	0.44
Carbofuran	266	0.41
1,2 – Dichlorobenzene	263	0.38
Hexachlorobutadiene	258	0.45
Δ - Nonylphenol	250	0.37
4-Dimethylaminoazobenzene	249	0.24
PCB – 1221	242	0.70
DDE	232	0.37
m-Xylene	230	0.75
Acridine yellow	230	0.12
Dibromochloropropane (DBCP)	224	0.51
Benzidine dihydrochloride	220	0.37
∃ - BHC	220	0.49
n-Butylphthalate	220	0.45
n-Nitrosodiphenylamine	220	0.37
Silvex	215	0.38
Phenanthrene	215	0.44
Dimethylphenylcarbinol	210	0.34
4 – Aminobiphenyl	200	0.26

Table 2 (continued)

Compound	$K(mg/g)(L/mg)^{1/n}$	l/n
∃ - Naphthol	200	0.26
Δ - Xylene	200	0.42
∀ - Endosulfan	194	0.50
Chlordane	190	0.33
Acenaphthene	190	0.36
4,4' Methylene-bis (2-chloroaniline)	190	0.64
Benzo[6]fluoranthene	181	0.57
Acridine orange	180	0.29
∀-Naphthol	180	0.32
Ethylbenzene	175	0.53
≅-Xylene	174	0.47
4,6-Dinitro-≅-cresol	169	0.27
∀-Naphthylamine	160	0.34
2,4-Dichlorophenol	157	0.15
1,2,4-Trichlorobenzene	157	0.31
2,4,6-Trichlorophenol	155	0.40
∃-Naphthylamine	150	0.30
2,4-Dinitrotoluene	146	0.31
2,6-Dinitrotoluene	145	0.32
4-Bromophenyl phenyl ether	144	0.68
Δ-Nitroaniline	140	0.27
1,1-Diphenylhydrazine	135	0.16
Naphthalene	132	0.42
Aldicarb	132	0.40
1-Chloro-2-nitrobenzene	130	0.46
p-Chlorometacresol	124	0.16
1,4-Dichlorobenzene	121	0.47
Benzothiazole	120	0.27
Diphenylamine	120	0.31
Guanine	120	0.40
1,3-Dichlorobenzene	118	0.45
Acenaphthylene	115	0.37
Methoxychlor	115	0.36
4-Chlorophenyl phenyl ether	111	0.26
Diethyl phthalate	110	0.27
Chlorobenzene	100	0.35
Toluene	100	0.45
2-Nitrophenol	99	0.34
Dimethyl phthalate	97	0.41
Hexachloroethane	97	0.38
2,4-Dimethylphenol	78	0.44
4-Nitrophenol	76	0.25
Acetophenone	74	0.44
1,2,3,4-Tetrahydronaphthalene	74	0.81
Adenine	71	0.38
Dibenzo[∀h]anthracene	69	0.75
Nitrobenzene	68	0.43
2,4-D	67	0.27

Table 2 (continued)

Compound	K(mg/g)(L/mg)$^{1/n}$	l/n
3,4-Benzofluoranthene	57	0.37
2-Chlorophenol	51	0.41
Tetrachloroethylene	51	0.56
≅-Anisidine	50	0.34
5-Bromouracil	44	0.47
Benzo[∀]pyrene	34	0.44
2,4-Dinitrophenol	33	0.61
Isophorone	32	0.39
Trichloroethylene	28	0.62
Thymine	27	0.51
5-Chlorouracil	25	0.58
N-Nitrosodi-n-propylamine	24	0.26
Bis(2-Chloroisopropyl)ether	24	0.57
1,2-Dibromoethene (EDB)	22	0.46
Phenol	21	0.54
Bromoform	20	0.52
1,2-Dichloropropane	19	0.59
1,2-$trans$-Dichloroethylene	14	0.45
cis-1,2-Dichloroethylene	12	0.59
Carbon tetrachloride	11	0.83
Bis(2-Chloroethyoxy)methane	11	0.65
Uracil	11	0.63
Benzo[g,h,i]perylene	11	0.37
1,1,2,2-Tetrachloroethane	11	0.37
1,2-Dichloropropene	8.2	0.46
Dichlorobromomethane	7.9	0.61
Cyclohezanone	6.2	0.75
1,1,2-Trichloroethane	5.8	0.60
Trichlorofluoromethane	5.6	0.24
5-Fluorouracil	5.5	1.0
1,1-Dichloroethylene	4.9	0.54
Dibromochloromethane	4.8	0.34
2-Chloroethyl vinyl ether	3.9	0.80
1,2-Dichloroethane	3.6	0.83
Chloroform	2.6	0.73
1,1,1-Trichloroethane	2.5	0.34
1,1-Dichloroethane	1.8	0.53
Acrylonitrile	1.4	0.51
Methylene chloride	1.3	1.16
Acrolein	1.2	0.65
Cytosine	1.1	1.6
Benzene	1.0	1.6
Ethylenediaminetetraacetic acid	0.86	1.5
Benzoic acid	0.76	1.8
Chloroethane	0.59	0.95
N-Dimethylnitrosamine	6.8×10^{-5}	6.6

The isotherms are for the compounds in distilled water, with different activated carbons. The values of K and 1/n should be used only as rough estimates of the values that will be obtained using other types of water and other activated carbon.

2-5. Dynamic Operation Testing. The following parameters must be considered when designing a pilot scale evaluation.
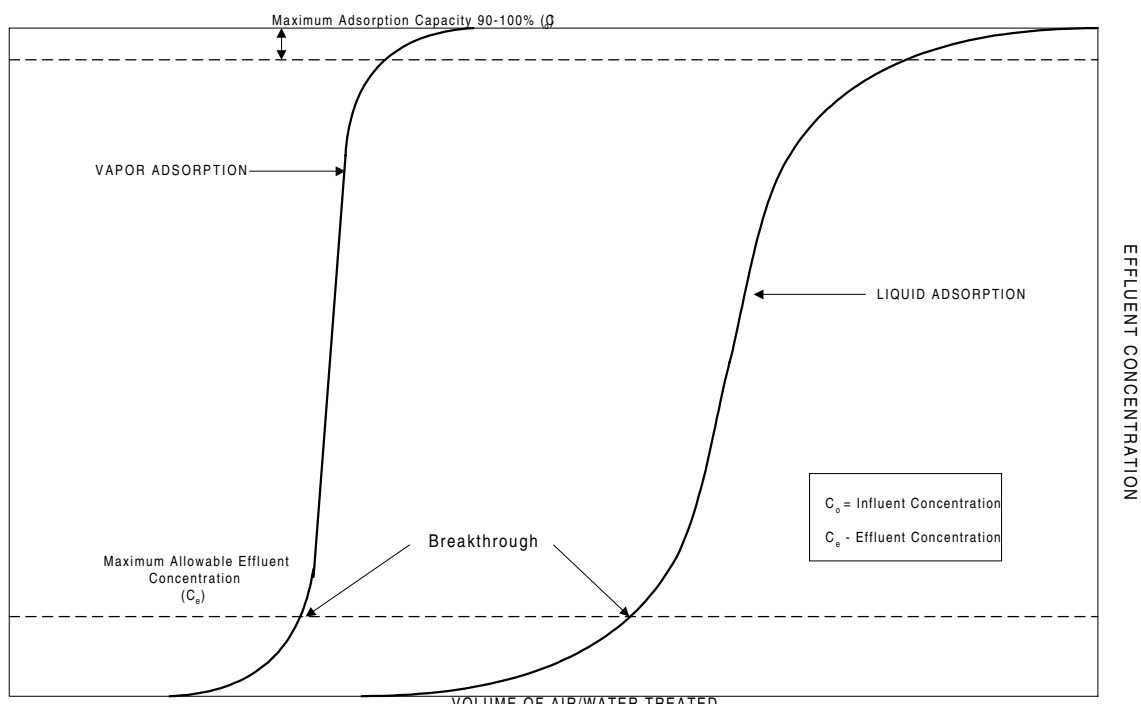
   a. Breakthrough Curves. The breakthrough curve can be defined as the "S" shaped curve that typically results when the effluent adsorbate concentration is plotted against time or volume. Breakthrough curves can be constructed for full scale, dynamic, or pilot testing. The breakthrough point is the point on the breakthrough curve where the effluent adsorbate concentration reaches its maximum allowable concentration, which often corresponds to the treatment goal. The treatment goal is usually based on regulatory or risk based numbers (see Figure 2-4).

   b. Mass Transfer Zone. The mass transfer zone (MTZ) is the area within the adsorbate bed where adsorbate is actually being adsorbed on the adsorbent. The MTZ typically moves from the influent end toward the effluent end of the adsorbent bed during operation. That is, as the adsorbent near the influent becomes saturated (spent) with adsorbate, the zone of active adsorption moves toward the effluent end of the bed where the adsorbate is not yet saturated. The MTZ is sometimes called the adsorption zone or critical bed depth. The MTZ is generally a band, between the spent carbon and the fresh carbon, where adsorbate is removed and the dissolved adsorbate concentration ranges from C_O to C_e.

      (1) The length of the MTZ can be defined as L_{MTZ}. When L_{MTZ} = bed depth, it becomes $L_{CRIT,}$ or the theoretical minimum bed depth necessary to obtain the desired removal.

      (2) As adsorption capacity is used up in the initial MTZ, the MTZ advances down the bed until the adsorbate begins to appear in the effluent. The concentration gradually increases until it equals the influent concentration. In cases where there are some very strongly adsorbed components, in addition to a mixture of less strongly adsorbed components, the effluent concentration very seldom reaches the influent concentration because only the components with the faster rate of movement through the adsorber are in the breakthrough curve. The MTZ is illustrated in Figure 2-5.

      (3) Adsorption capacity is influenced by many factors, such as flow rate, temperature, and pH (liquid phase). The adsorption column may be considered exhausted when the effluent adsorbate concentration equals 95–100% of the influent concentration. This is illustrated in Figure 2-5.

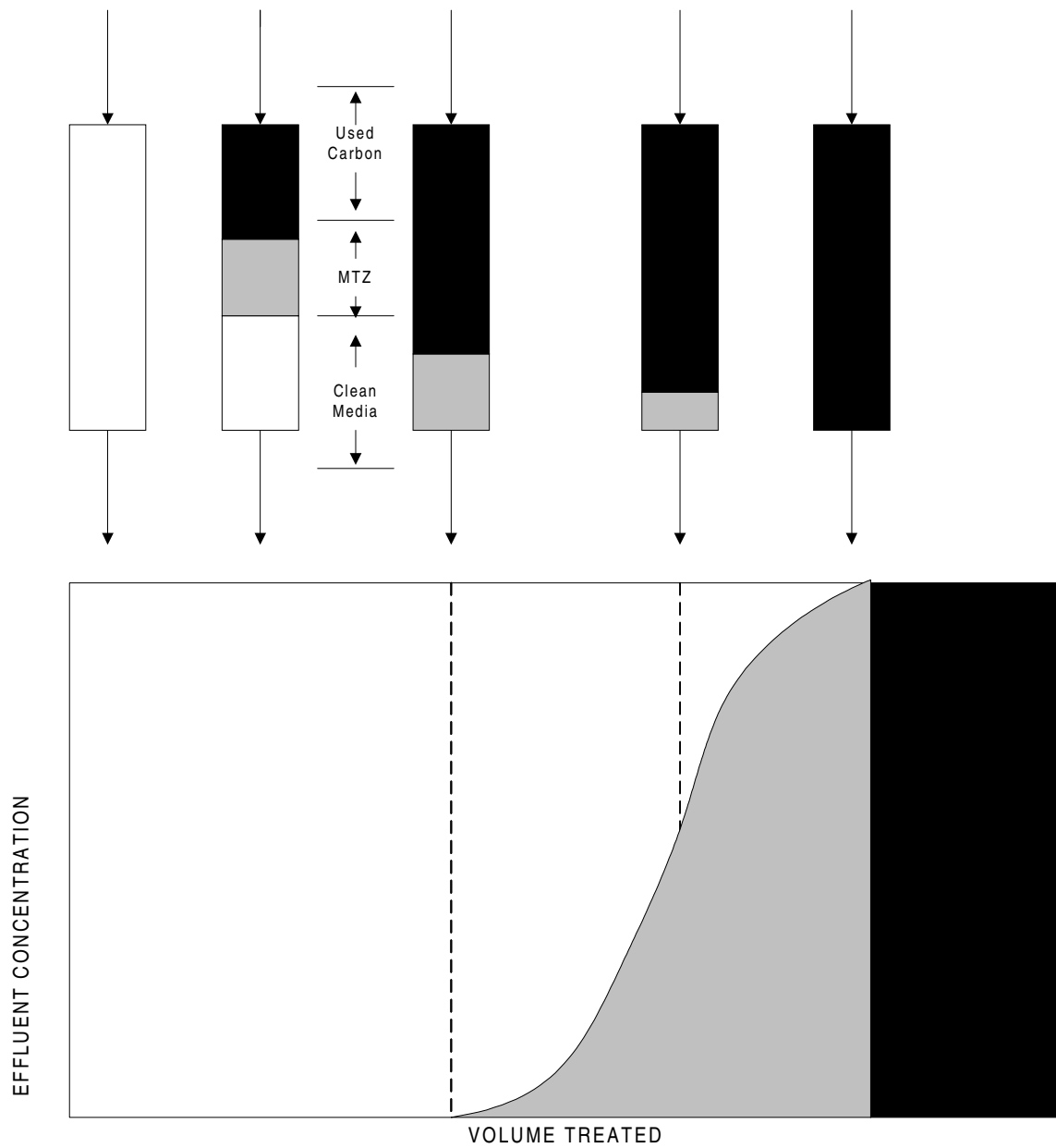**Figure 2-4. Comparison of idealized vapor and liquid breakthrough curves.**

Figure 2-5. Adsorption column mass transfer zone and idealized breakthrough zone.

2-6. Pilot Tests. Pilot studies are almost always recommended for liquid phase applications. After bench scale isotherm tests have provided "proof of concept" data for the media (e.g. GAC), pilot testing should be used to determine if the site-specific conditions will interfere with the media and to test solutions for managing the interferences. Pilot tests will verify the characteristics of the breakthrough curve at selected process parameters, such as surface loading rates and empty bed contact times. For example, there may be competition for adsorption sites among different compounds in the waste stream. Analysis for these competing compounds may not be routinely conducted, so their presence and concentration in the waste stream would not be known. This type of competition can be minimized by selecting a product that selectively adsorbs only the compounds of concern. Also, variations in the water chemistry (pH, buffer capacity, etc.) may affect the performance and capacity of the adsorbent. Pilot tests should also be used to generate scale up factors for the full-scale design.

a. Several manufacturers have mobile pilot systems, and most manufacturers will (for a fee) conduct pilot testing of waste streams for customers. It may be possible to negotiate package deals, where testing costs would be reduced if the pilot scale manufacturer were selected for the full-scale project.

b. There are two basic types of column tests that can be run to determine the parameters mentioned above: the standard pilot column test, and the high pressure minicolumn test. The standard pilot column test consists of four or more carbon columns in series. The columns are 50 to 150 mm (2 to 6 in.) in diameter, generally contain 1.8 to 3.6 m (2 to 4 ft) of GAC, and operate in either the downflow or upflow mode. If suspended solids are a concern for the full scale operation, downflow operation with backwashing capabilities to remove filtered solids is generally the best option. In an upflow mode, the solids would likely plug most distributors. The upflow operation typically generates carbon fines and, thus, gray water. Downflow mode is generally preferred for liquid streams, unless they are susceptible to biological fouling. Four pilot columns are generally selected to ensure that the wave front or mass transfer zone can be tracked through the columns. The column operating characteristics (e.g., surface loading rate, detention time, vertical velocity through the bed) should be similar to those expected in the full scale system. Typically, in full-scale water-treatment applications, except large potable water plants that have adsorbers operating in parallel, the mass transfer zone is contained in the first adsorber in a system having two adsorbers in series. In unique process applications, where the contact time is several hours, three beds in series may be necessary. There are very few systems with four vessels in series. Methods to apply the data to other conditions, such as the bed depth service time (BDST), and Bohart Adams relationships and operating line method are described in various references (Benefield, 1982; Faust and Aly, 1987; AWWA, 1997; Erskine and Schuliger, 1971) A typical pilot column configuration is shown in Figure 2-6.

c. A high pressure water minicolumn (HPMC) test or small scale column test was developed to reduce the length of time required to obtain operational data from a column test (see Figure 2-6). A traditional column test could take a month or more to run, while a HPMC test can be completed in a matter of hours. The HPMC process used is generally manufacturer-specific but depends largely upon mathematical modeling, given the particle size used in the HPMC and test parameters and database of past tests, as well as the experience of the individual interpreting the test data. The apparatus consists of a 0.4- to 2.0-mm-diameter column with a bed depth ranging from 10 to 100 mm. It uses a sample of the subject test GAC, crushed to pass a 60×80 mesh or smaller. The minicolumn tests are generally about one order of magnitude less expensive, can be completed quickly, require a smaller volume of water, have minimal chance for biological or other deterioration of the sample, and multiple carbons can easily be tested to obtain the most effective design. Additional information can be obtained from testing labs, carbon manufacturers, and *AWWA Water Quality and Treatment* (1997). A typical apparatus is shown in Figure 2-7. A procedure for estimating GAC performance using a slightly larger diameter column of 25.4 mm $\pm$ 0.1 mm is identified in ASTM D3922.

2-7. Spent Carbon Management. Spent carbon has the potential to be regulated for disposal under the *Resource Conservation and Recovery Act* (RCRA). Spent carbon used to treat listed hazardous waste or which exhibits a RCRA hazardous characteristic (ignitable, corrosive, reactive, or exceeding toxicity characteristic leaching procedure threshold levels) must be managed as a hazardous waste after use in an adsorption process and be manifested to a permitted RCRA Treatment, Storage or Disposal Facility (TSDF). This TSDF may be either a disposal or a regeneration facility. If it is managed on-site under CERCLA, a permit is not required, but substantive requirements applicable to TSDFs must be met. On the other hand, if it was not used to treat listed waste, and it does not exhibit a hazardous characteristic, then the spent carbon can be disposed of or regenerated without being subject to RCRA permitting or manifesting requirements. The determination of RCRA status is the legal responsibility of the generator (operator/owner) of the treatment facility. Coordinate with carbon manufacturers, or your local regulatory specialist, for additional information.

2-8. Safety Concerns. The safety concerns unique to carbon adsorption are discussed in EM 1110-1-4007.
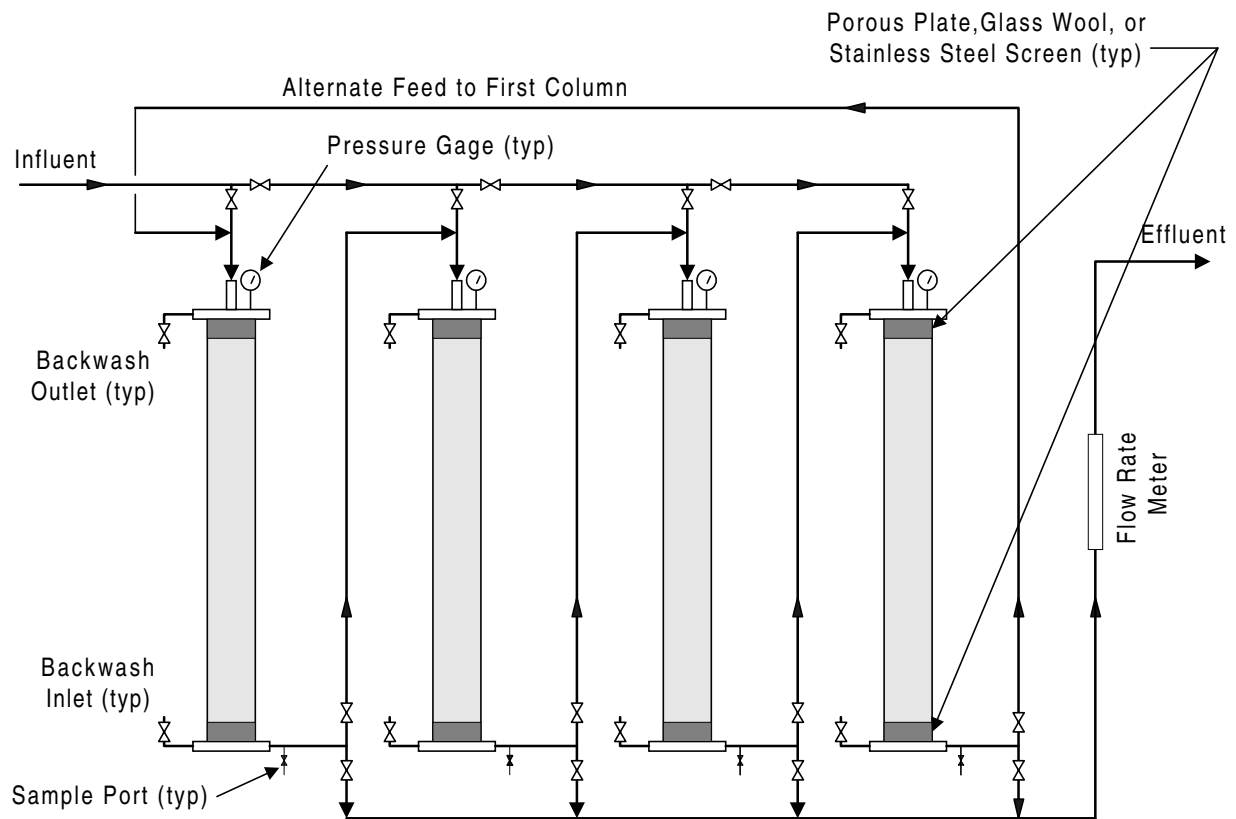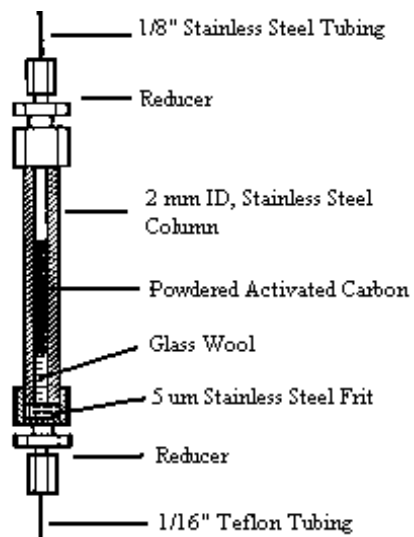
Figure 2-6. Typical pilot column apparatus.

Figure 2-7. Minicolumn apparatus.